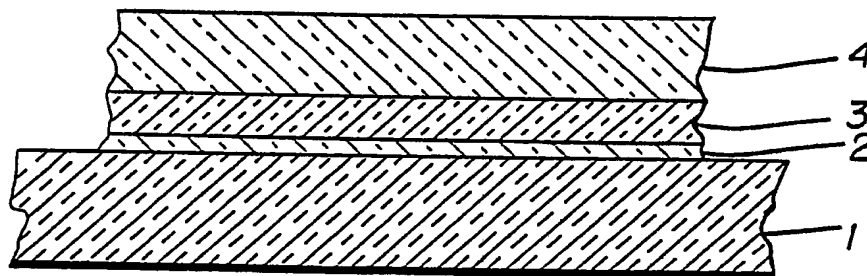


PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : B32B 9/00, 7/02, C23C 16/02	A1	(11) International Publication Number: WO 92/06843 (43) International Publication Date: 30 April 1992 (30.04.92)
(21) International Application Number: PCT/US91/07209 (22) International Filing Date: 1 October 1991 (01.10.91) (30) Priority data: 600,210 18 October 1990 (18.10.90) US (71) Applicant: DIAMONEX, INCORPORATED [US/US]; 7150 Windsor Drive, Allentown, PA 18106-9328 (US). (72) Inventors: KIMOCK, Fred, M. ; 2961 Magnolia Avenue, Macungie, PA 18062 (US). KNAPP, Bradley, J. ; 2124 Highland Street, Allentown, PA 18104 (US). FINKE, Steven, James ; RD #3, Box 485, Kutztown, PA 19350 (US).		(74) Agents: McCUBBREY, J., Bruce et al.; Suite 2700, One Post Street, San Francisco, CA 94104-5231 (US). (81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European pa- tent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (Euro- pean patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i> <i>With amended claims.</i>

(54) Title: ABRASION WEAR RESISTANT POLYMERIC SUBSTRATE PRODUCT**(57) Abstract**

A substantially optically transparent coated substrate product (1) with a highly adherent, abrasion-resistant diamond-like hard carbon coating (4) is disclosed. The substrate product is comprised of a polymeric substrate (1), and adhesion-mediating polysiloxane polymer layer (2), one or more intermediate layers (3) and an outer layer of diamond-like hard carbon (4). The invention also allows for the production of adherent thin film interference layer coatings (i.e. quarter wavelength stacks and anti-reflection coatings) using diamond-like hard carbon as the high refractive index layer and the interlayer(s) as the low refractive index layer or, alternatively, using diamond-like hard carbon as the low refractive index layer and the interlayer(s) as the high refractive index layer. The substrate product is useful as optical and sunglass lenses.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LI	Liechtenstein	SU ⁺	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
DE ⁺	Germany	MC	Monaco	US	United States of America
DK	Denmark				

⁺ Any designation of "SU" has effect in the Russian Federation. It is not yet known whether any such designation has effect in other States of the former Soviet Union.

WO 92/06843

PCT/US91/07209

-1-

**ABRASION WEAR RESISTANT
POLYMERIC SUBSTRATE PRODUCT**

FIELD OF THE INVENTION

5 This invention relates generally to coated
substrate products. More particularly, the invention
relates to a substantially optically transparent coated
substrate product comprised of a polymeric parent
substrate, one or more interlayers and a diamond-like
10 carbon layer, and to a method for producing same.

BACKGROUND OF THE INVENTION

 The properties of polymers (i.e., plastics) make
them ideal substrate materials for use in many
applications. In particular, optically transparent
15 plastics such as polycarbonate, CR-39[®] (allyl diglycol
carbonate) and acrylics have become widely accepted
materials for use as optical lenses because of their
light weight and ease of molding compared to glass.
Polycarbonate also has superior impact resistance
20 compared to glass. However, a major drawback with
plastic substrates, particularly polycarbonate, is their
poor scratch and abrasion resistance.

 Various methods have been employed to enhance the
abrasion wear resistance of plastic substrates. For
25 example, many commercial plastic ophthalmic and sunglass
lenses are coated with either organic acrylate-type
polymer coatings or polysiloxane-type polymer coatings.
(See, S. Herbert, Industrial Diamond Review, Feb. 1984,
at p.77.) Although these polymer coatings offer a
30 significant improvement in abrasion resistance relative
to the uncoated plastic lens, the perceived abrasion
resistance of the coated plastic lens compared to a glass
lens is still poor.

 Glass and silicon dioxide have also been employed
35 as coatings on plastic substrates to improve the abrasion
resistance. Illustrative are Great Britain Patent No.

WO 92/06843

PCT/US91/07209

-2-

1,335,065, and U.S. Patent Nos. 3,458,342 and 4,328,646. However, the absence of an intermediate layer between the glass or silicon dioxide layer and the plastic substrate often results in the glass or silicon dioxide coating
5 spalling or cracking when the substrate is subjected to thermal cycling.

Several prior art techniques disclose the use of an intermediate layer between the substrate and the glass or silicon dioxide outer layer to improve adhesion of the
10 outer layer. For example, U.S. Patent 4,190,681, issued to Hall, et al., discloses an evaporative deposition technique of a glass layer disposed on top of an intermediate layer of an acrylic-type polymer which has in turn been coated onto a polycarbonate substrate. U.S.
15 Patent No. 4,200,681, also issued to Hall, et al., discloses the vapor deposition of a top layer of silicon dioxide onto an intermediate primer layer which in turn has been deposited on the surface of a polycarbonate substrate. However, this particular evaporative
20 technique of applying a layer of silicon dioxide is often undesirable for several reasons. First, this technique suffers from inadequate adhesion of the silicon dioxide or glass layer, due to (i) the relatively low reactivity of the evaporated silicon oxide film-forming species, and
25 (ii) insufficient bond strength between the silicon dioxide layer and the underlying carbonaceous acrylic polymer layer. Second, the individual particles of silicon dioxide may evaporate and later condense on the coating surface at rates which vary with the particular
30 site of deposition, resulting in a non-uniform glass surface often characterized by pits, pinholes, and other imperfections.

U.S. Patent No. 3,713,869, teaches the deposition of an intermediate layer polymerized by glow discharge
35 onto a polycarbonate surface. A hard inorganic glass layer is then vaporized by an electron beam gun onto the

WO 92/06843

PCT/US91/07209

-3-

intermediate layer in a manner similar to that used by Hall, et al. European Patent Application No. 0,266,225 further discloses a coating in which the plastic substrate is first coated with a silicon-based layer which is overcoated by a top layer of silicon dioxide. U.S. Patent No. 4,842,941 discloses a polycarbonate substrate with an interfacial layer of resinous composition, and an abrasion-resistant top layer applied by plasma-enhanced chemical vapor deposition. U.S. Patent No. 4,341,841 discloses an article with a multi-layer protective coating, comprising a substrate and two protective layers, one being a vacuum coated ceramic layer, and one being a resinous layer, coated in any order. Although each of these prior art techniques have resulted in limited improvement in the adhesion between the glass or silicon dioxide coating and the substrate, and ultimately the wear resistance of the coated substrate product, the prior art techniques do not contemplate a diamond-like carbon ("DLC") outer layer, nor address the optimum method for obtaining an adherent DLC layer on a polycarbonate substrate.

In all of the aforementioned prior art techniques, the abrasion resistance of the coated plastic substrate has been unsatisfactory because of the limited hardness of the silicon dioxide or glass coating. Additional problems are also encountered by thin oxide coatings. Due to incomplete oxidation or inhomogeneous chemical bonding which is characteristic of oxide films, the films are susceptible to chemical reaction and damage by salt water. This is a particular disadvantage for eyeglass or sunglass lenses which are exposed to perspiration or ocean spray. Finally, under thermal cycling or flexing, the oxide coatings are susceptible to cracking and peeling.

There are also teachings of "mixed phase" or "gradient" inorganic hard coatings for plastic substrates

WO 92/06843

PCT/US91/07209

-4-

which can be found in the prior art. For example, U.S. Patent No. 4,830,873, issued to Benz, et al., discloses a process for applying a transparent layer onto the surface of a plastic element by first polymerizing an organic vapor and subsequently introducing additives such as oxygen, hydrocarbon compounds, or nitrogen-containing compounds to the vapor to form a layer with increased hardness. International Patent Application No. W089/01957 discloses a method for depositing an abrasion-resistant coating comprising the plasma-enhanced chemical vapor deposition of a coating characterized by a gradual transition from a composition consisting essentially of an interfacial material to a composition consisting essentially of an abrasion-resistant material. Further, U.S. Patent No. 4,777,090, discloses a product which has a disordered carbon coating at the substrate-coating interface and a relatively ordered portion composed of either carbon or silicon dioxide away from the substrate-coating interface. These prior art techniques similarly do not teach the deposition of a hard DLC layer, nor discuss the formation of a discrete multilayer coating structure with a polycarbonate substrate and an adherent DLC outer layer.

There are, however, several prior art references which teach the direct deposition of hard DLC films onto plastic substrates to improve abrasion resistance. Illustrative are U.S. Patent Nos. 4,663,183, 4,770,940, 4,783,361, 4,698,256 and 4,877,677, and European Application Nos. 0,280,215 and 0,278,480. These prior art references do not teach the use of interlayer materials which have been found to be essential to achieve satisfactory adherence of the DLC film.

There are also prior art references which teach the deposition of hard DLC films onto plastic substrates with the use of limited interlayer materials. For example, U.S. Patent No. 4,661,409, issued to Kieser, et

WO 92/06843

PCT/US91/07209

-5-

al., discloses a substrate having an amorphous carbon coating and an adhesion-mediating interlayer of a siloxane or silazane polymer between the carbon film and the substrate. U.S. Patent No. 4,569,738, also issued to
5 Kieser, et al., discloses a microwave discharge process for depositing the siloxane or silazane polymer and amorphous carbon layers on the substrate. However, in each of these references only intermediate layers of microwave discharge-deposited siloxane and silazane
10 polymers are discussed.

Although DLC coatings possess excellent optical properties and exhibit excellent resistance to abrasion and chemical attack, DLC coatings have not been widely applied to plastic substrates (including lenses) to date
15 for several reasons. First, while DLC coatings are indeed very hard, they are also brittle when thin. Thus, when applied to soft substrates such as plastics, the DLC coating can crack and/or be crushed into the substrate when a high load or force is applied to the surface of
20 the substrate. This mechanism is also responsible for the apparent scratching of the DLC coating from the surface of plastic substrates in severe abrasive environments.

Second, the adhesion of DLC coatings to plastic
25 substrates has been poor due to the high internal stress associated with the DLC coatings. This poor adhesion has been especially evident during cooling of DLC coated plastic substrates from elevated temperatures. There is also a significant difference in the thermal expansion
30 coefficients between the DLC coating and the plastic substrate. Thus, during thermal cycling the weak adhesive bonding strength at the DLC-plastic interface is overwhelmed by the forces generated by expansion and contraction, and hence, the DLC coating cracks and
35 delaminates.

It is therefore an object of the present

WO 92/06843

PCT/US91/07209

-6-

invention to provide a plastic substrate with hard coated surface layers, such as diamond-like carbon, firmly adhered thereto, thereby to prevent undesirable separation or crack formation, while at the same time
5 providing excellent hardness and resistance to abrasion, chemical attack and impact.

It is a further object of the present invention to provide an abrasion-resistant plastic substrate with increased ease of cleaning.

10 It is a further object of the present invention to provide a plastic substrate with a diamond-like hard carbon coating which combines the ability to reflect decorative colors without sacrificing the aforementioned objects.

15 It is a further object of the present invention to provide a method for depositing an adherent coating incorporating high refractive index diamond-like hard carbon layers in an alternating layer stack along with at least one other material of substantially different
20 refractive index in order to produce thin film interference coatings such as quarter wavelength stacks.

It is a further object of this invention to provide a low cost and efficient process for producing a plastic substrate with superior abrasion wear resistance
25 and reduced chemical reactivity.

SUMMARY OF THE INVENTION

The disclosed abrasion wear resistant coated substrate product substantially reduces or eliminates the disadvantages and shortcomings associated with the prior
30 art techniques. The invention discloses a substantially optically transparent composite structure which comprises a polymeric parent substrate, one or more intermediate layers and a diamond-like carbon layer. The invention also discloses a method for fabricating the coated
35 substrate product.

According to the method, the substrate surface is

WO 92/06843

PCT/US91/07209

-7-

initially chemically de-greased. In the second step, the substrate is coated with a polysiloxane polymer layer by a flow, dip, spray, or other conventional solution-based coating process. After the polysiloxane polymer layer is thermally cured, the coated surface is chemically cleaned. The substrate surface is then sputter-etched with energetic gas ions to assist in the removal of residual hydrocarbons, as well as alkali metals and other additives. After sputter-etching, one or more interlayers are chemically vapor deposited on the substrate, followed by the deposition of a diamond-like carbon layer. Once the requisite number of interlayers and diamond-like carbon layers have been deposited, the coated substrate is cooled and removed from the reactor.

BRIEF DESCRIPTION OF THE DRAWINGS

Further features and advantages will become apparent from the following and more particular description of the preferred embodiment of the invention, as illustrated in the accompanying drawings, in which like reference characters generally refer to the same parts or elements throughout the views, and in which:

Figure 1 is a cross-sectional view of the coated substrate product in accordance with the present invention;

Figure 2 is a cross-sectional view of the coated substrate product in accordance with a further embodiment of the present invention; and

Figure 3 is a cross-sectional view of the coated substrate product in accordance with a still further embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention, the disclosed abrasion wear resistant coated substrate product substantially reduces or eliminates the disadvantages and shortcomings associated with the prior art techniques. As illustrated in Figures 1-3, the

WO 92/06843

PCT/US91/07209

-8-

disclosed invention is a substantially optically transparent composite structure which comprises a polymeric parent substrate, one or more intermediate layers (interlayers) and a diamond-like carbon layer. By the term of "substantially optically transparent", it is intended to mean transparent to light in the visible region of the electromagnetic spectrum, which is generally between 350 nanometers and approximately 750 nanometers wavelength. A highly important technical advantage of the invention is that the resultant multilayer composite structure has all of the typical attributes of plastics, such as high tensile and impact strength, while also exhibiting excellent resistance to wear and chemical attack.

In the preferred embodiment form of the invention, as illustrated in Figure 1, the polymeric parent substrate 1 is coated with an adhesion-mediating polysiloxane polymer layer 2 by a conventional dip, flow, spray, or other solution-based coating process. In accordance with the invention, it has been found that adherence of diamond-like carbon ("DLC") film to a polymeric substrate is significantly improved, resulting in decidedly better product lifetime, when one applies an adherence transmitting intermediate layer, such as a polysiloxane polymer, between the polymeric substrate 1 and the diamond-like carbon layer 4 (i.e. inorganic hard layer). The enhanced adhesion between the polymeric substrate and a diamond-like carbon layer 4 is due, in part, to the fact that the elastic modulus and thermal expansion coefficient of the polysiloxane layer 2 is generally intermediate between that of the plastic substrate 1 and the diamond-like carbon layer 4, resulting in reduced expansion mismatch between the substrate 1 and the diamond-like carbon layer 4. Polysiloxane polymers are formed from monomers such as bi-, tri-, and tetra-function silanes, in which silicon

WO 92/06843

PCT/US91/07209

-9-

atoms are bonded to hydrogen atoms, alcohol functional groups, or alkoxy functional groups. By conventional condensation polymerization (so-called thermal curing process) these monomeric mixtures are converted to

5 oligomers, and subsequently into a 3-dimensional network polymer by elimination (or condensation) of water or alcohols. The degree of crosslinking in the polysiloxane polymer coating is determined by the amount of tri-, and

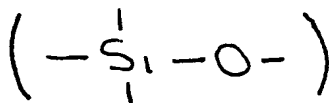
10 tetra-functional monomers and/or the amount of pre-polymerized crosslinking agents having reactive end groups which are included in the mixture. Polysiloxane polymer coatings can also incorporate additives such as resins (nylon, epoxy, melamine, etc.), hardners, flow control agents, diluents, thickeners, catalysts, dyes,

15 pigments, colloidal suspensions of silicon dioxide and other oxide materials which can be used to modify the properties of the coating. Polysiloxane polymer layers are indeed known per se, but not known has been their excellent suitability as an intermediate layer for

20 improving adherence (primer) between plastics and DLC coatings.

By the term of "polysiloxane polymer", it is thus intended to mean a 3-dimensional network condensation polymer in which silicon atoms are bonded to 2-4 oxygen

25 atoms. In the case of silicon bonded to 2 oxygen atoms, the oxygen atoms are inter-bonded to silicon atoms and these are a part of a



30 repeating unit in a linear sense, forming linear runs of the polymer, and where the third and fourth bonding positions on the silicon atoms are occupied by unreactive organic functional groups, either alkyl or aryl groups.

35 Furthermore, there will be some number of silicon atoms bonded to 3 oxygen atoms, and a lesser number of silicon

WO 92/06843

PCT/US91/07209

-10-

atoms bonded to 4 oxygen atoms. In each case, those oxygen atoms bonded to silicon atoms are the sites for linking linear runs of the polymer to form a 3-dimensional network.

5 The adhesion-mediating polysiloxane polymer layer 2 can be from 1 to 20 microns in thickness. In the preferred embodiment form of the invention; the adhesion-mediating layer is at least 3 microns thick. It has been found that a critical polysiloxane layer thickness of at
10 least 3 microns is necessary to provide the diamond-like carbon layer 4 with adequate mechanical support under high loads. This added support greatly reduces "crushing" of the diamond-like carbon layer 4 into the substrate 1, allowing the amount of abrasion protection
15 offered by the diamond-like carbon layer 4 to be greatly increased.

 Following deposition of the adhesion-mediating polysiloxane polymer layer, a first interlayer 3 is chemically vapor deposited onto the substantially
20 optically transparent polymeric parent substrate 1. By the term of "chemically vapor deposited", it is intended to mean materials deposited by vacuum deposition processes, including thermal evaporation, electron beam evaporation, magnetron sputtering, and ion beam
25 sputtering from solid precursor materials; thermally-activated deposition from reactive gaseous precursor materials; and glow discharge, plasma, or ion beam deposition from gaseous precursor materials. Preferably, the first interlayer 3 is deposited onto the parent
30 substrate 1 by ion beam sputtering or magnetron sputtering when dense layers exhibiting compressive stress are desired, or by electron-beam evaporation when layers exhibiting tensile stress are desired, as discussed more fully herein.

35 The first interlayer 3 generally comprises a substantially optically transparent material devoid of

WO 92/06843

PCT/US91/07209

-11-

alkali metal atoms and fluorine, and capable of forming a strong chemical bond to the coated substrate 1 and the diamond-like carbon layer 4. By the term of "strong chemical bond", it is intended to mean that the

5 interlayer is composed of a significant amount of an element or elements which are capable of undergoing a chemical reaction with carbon to form carbide-bonding. The absence of alkali metals and fluorine is essential to achieve a highly adherent interface between the first

10 interlayer 3 and the diamond-like carbon layer 4. Thus, the first interlayer 3 must also have the property of providing a barrier to diffusion of alkali metals and additives from the parent substrate 1 to the diamond-like carbon layer 4.

15 The first interlayer 3 can be from 5 Å to 10,000 Å in thickness, preferably at least 10 Å thick, and may comprise silicon oxide, silicon dioxide, yttrium oxide, germanium oxide, hafnium oxide, tantalum oxide, titanium oxide, zirconium oxide tungsten oxide,

20 molybdenum oxide, boron oxide or mixtures thereof. By the term "oxide", it is intended to mean a stoichiometrically oxidized material, or a partially oxidized material which contains excess metal atoms, or is deficient in oxygen. The first interlayer may further

25 comprise silicon nitride, titanium nitride, tantalum nitride, hafnium nitride, zirconium nitride, boron nitride, tungsten nitride, molybdenum nitride, silicon carbide, germanium carbide and mixtures thereof. By the term "nitride", it is intended to mean a material

30 composed of a stoichiometric amount of nitrogen or a material which either contains excess nitrogen atoms, or is deficient in nitrogen. By the term "carbide", it is intended to mean a material composed of a stoichiometric amount of carbon or a material which either contains

35 excess carbon atoms, or is deficient in carbon.

In the preferred embodiment form of the

WO 92/06843

PCT/US91/07209

-12-

invention, the first interlayer 3 comprises silicon dioxide. Silicon dioxide is the preferred interlayer material due to (i) its chemical similarity with the polysiloxane polymer adhesion-mediating layer 2 and the resultant affinity to form a strong chemical bond thereto and (ii) its ability to form an excellent chemical bond to diamond-like carbon. In accordance with the invention, it has been found that the thickness of the silicon dioxide first interlayer 3 should be from 200 Å to 2000 Å to achieve optimum adhesion of the diamond-like carbon layer 4. Generally, the necessary thickness of the silicon dioxide interlayer 3 is dependent upon the nature of the polymeric substrate material, the physical characteristics of the diamond-like carbon layer 4 bonded to the silicon dioxide first interlayer 3, and the degree of adhesion required for the particular application. For example, it has been found that when silicon dioxide layers less than approximately 400 Å are employed as coatings over polycarbonate substrates, diamond-like carbon layers of thicknesses greater than 850 Å will undergo adhesion failure when the substrate is thermally cycled. However, silicon dioxide layers of approximately 200 Å are sufficient to promote excellent adhesion with substrates exhibiting a lower thermal expansion coefficient (i.e. CR-39[®] and acrylic plastics) and/or diamond-like carbon layers of thickness less than 850 Å. In accordance with the invention, it is therefore preferable that the silicon dioxide first interlayer 3 be at least 200 Å thick.

Following deposition of the first interlayer 3 onto the coated parent substrate 1, the diamond-like carbon layer 4 is chemically vapor deposited onto the coated substrate. The diamond-like carbon layer 4 can be from 10 Å to 10 micrometers in thickness. Preferably, the diamond-like carbon layer 4 is at least 200 Å thick.

To further enhance the abrasion wear resistance

WO 92/06843

PCT/US91/07209

-13-

of the structure, more than one interlayer or a plurality of alternating interlayers 3 and diamond-like carbon layers 4 may be deposited onto the parent substrate 1, as shown in Figure 2. In a further envisioned embodiments of the invention not shown, the structure also may comprise a parent substrate 1, an adhesion-mediating layer 2, two or more different interlayers; a first diamond-like carbon layer 4, a first interlayer 3 and a second diamond-like carbon layer 4. It has been found that such arrangements allow for the deposition of a greater total thickness of DLC material, which provides a further increase in abrasion resistance.

However, as the thickness of the coated substrate product increases, control of the stresses in the respective diamond-like carbon layer(s) 4 and the interlayer(s) 3 becomes imperative. For example, if the interlayer 3 (e.g. silicon dioxide) is deposited onto the parent substrate 1 with an excessive tensile stress, the interlayer 3 may craze or crack. If the interlayer 3 is deposited onto the parent substrate 1 with an excessive compressive stress, problems with the adherence of the interlayer 3 and diamond-like carbon layer(s) 4 may be encountered. Therefore in the preferred embodiment form of the invention, the compressive stress in the interlayer(s) 3 is less than the compressive stress in the diamond-like carbon layer(s) 4; more preferably, the compressive stress in the interlayer(s) 3 is intermediate between the compressive stress of the diamond-like carbon layer(s) 4 and the adhesion-mediating layer 2.

Alternatively, the interlayer(s) 3 may be deposited onto the parent substrate 1 under tensile stress. This may be achieved by evaporative deposition of the interlayer(s) 3. The advantage of depositing the interlayer(s) 3 under tensile stress would be that the tensile stress in the interlayer(s) 3 would tend to cancel out the compressive stress in the diamond-like

WO 92/06843

PCT/US91/07209

-14-

carbon layer(s) 4, allowing for a much thicker composite structure.

In accordance with a further aspect of the invention, the modulus of elasticity and hardness of the interlayer(s) 3 is preferably less than the modulus of elasticity and hardness of the diamond-like carbon layer 4; more preferably, the modulus of elasticity of the interlayer(s) 3 is intermediate that of the diamond-like carbon layer 4 and the adhesion-mediating layer 2, and the hardness of the diamond-like carbon layer 4 is at least twice as hard as the underlying interlayer(s) 3. With this particular arrangement, the impact resistance of the parent substrate 1 will be significantly enhanced.

In another embodiment of the invention, as illustrated in Figure 3, a second interlayer 5 is chemically vapor deposited onto the coated substrate 1 and positioned such that the second interlayer 5 is disposed between the first interlayer 3 and the diamond-like carbon layer 4. The second interlayer 5 would similarly comprise a substantially optically transparent material devoid of alkali metal atoms and fluorine, and capable of forming a strong chemical bond to the first interlayer 3 and the diamond-like carbon layer 4. The second interlayer 5 may be from 5 Å to 10,000 Å in thickness, preferably at least 10 Å thick, and comprise a substantially optically transparent silicon nitride, titanium nitride, tantalum nitride, tungsten nitride, molybdenum nitride, hafnium nitride, zirconium nitride, boron nitride, yttrium oxide, germanium oxide, hafnium oxide, silicon oxide, silicon dioxide, tantalum oxide, titanium oxide, zirconium oxide, tungsten oxide, molybdenum oxide, boron oxide, silicon carbide, germanium carbide and mixtures thereof.

In the preferred embodiment form of the invention, the second interlayer 5 would similarly comprise silicon dioxide. As previously discussed, the

WO 92/06843

PCT/US91/07209

-15-

silicon dioxide second interlayer 5 may be from 200 Å to 2000 Å in thickness, preferably at least 200 Å thick.

Since the second interlayer 5 provides a diffusion barrier for alkali metal atoms, fluorine and/or any additional additives which would adversely effect the adherence of the diamond-like carbon layer 4 and since the second interlayer 5 is capable of forming a strong chemical bond with diamond-like carbon, the first interlayer 3 could further comprise a substantially optically transparent aluminum oxide, cerium oxide, tin oxide, thorium oxide, lithium oxide, sodium oxide, potassium oxide, rubidium oxide, cesium oxide, francium oxide, beryllium oxide, magnesium oxide, calcium oxide, strontium oxide, cerium oxide, radium oxide, barium fluoride, cerium fluoride, magnesium fluoride, thorium fluoride, calcium fluoride, neodymium fluoride, lead fluoride, sodium fluoride, lithium fluoride, zinc selenide, zinc sulfide and mixtures thereof.

The second interlayer 5 may alternatively comprise a substantially optically transparent metallic material capable of reflecting visible light and capable of forming a strong chemical bond with the first interlayer 3 and the diamond-like carbon layer 4, selected from the following two groups. In the first group, the metallic material may consist of silicon, germanium, hafnium, molybdenum, tungsten, yttrium, tantalum, titanium and zirconium. These metallic materials all form a strong chemical bond to the diamond-like carbon layer 4.

The second group of metallic materials comprises vanadium, niobium, chromium, manganese, rhenium, technetium, iron, cobalt, iridium, rhodium, nickel, palladium, platinum, copper, silver, gold, zinc, ruthenium, indium, aluminum, tin, osmium, thallium, lead, antimony, bismuth and polonium. Preferably, the second interlayer 5 comprises rhenium, iridium, tin, indium,

WO 92/06843

PCT/US91/07209

-16-

aluminum, nickel, iron, chromium, copper, gold, silver and platinum. Although these materials will provide a diffusion barrier to alkali metal atoms and fluorine, they will not form a strong carbide bond with the diamond-like carbon layer 4. Therefore, if any of these metallic materials are selected for the second interlayer 5, a third interlayer (not shown) must be disposed between the second interlayer 5 and the diamond-like carbon layer 4. The third interlayer would similarly be from 5 Å to 10,000 Å in thickness, preferably at least 10 Å thick, and comprise a substantially optically transparent material devoid of alkali metal atoms and fluorine and selected from the group consisting of silicon nitride, titanium nitride, tantalum nitride, tungsten nitride, molybdenum nitride, hafnium nitride, zirconium nitride, boron nitride, yttrium oxide, germanium oxide, hafnium oxide, silicon oxide, silicon dioxide, tantalum oxide, titanium oxide, zirconium oxide, tungsten oxide, molybdenum oxide, boron oxide, silicon carbide, germanium carbide and mixtures thereof. In the preferred embodiment, the third interlayer would comprise silicon dioxide with a thickness of at least 200 Å (as previously discussed). Although it is not necessary, this third interlayer may be employed with the aforementioned first group of metallic materials.

The metallic second interlayer 5 can be from 5 Å to 1000 Å in thickness. Preferably, the metallic second interlayer 5 is at least 25 Å thick.

The thickness of the diamond-like carbon layer(s) 4, and interlayer(s) 3 which are applied over the metallic interlayer 5 can be precisely controlled to produce desired reflected colors such as gold, purple, blue, red, orange, green, etc. In this way, a plastic substrate (such as an optical sunglass lens) can be produced which combines the features of a controlled reflected color with the abrasion wear resistance of the

WO 92/06843

PCT/US91/07209

-17-

diamond-like carbon coating of the present invention.

In yet another envisioned embodiment of the invention not shown, the embodiment illustrated in Figure 3 and discussed above may be provided with a second composite layer comprising a first interlayer 3 and a diamond-like carbon layer 4. The resultant multilayer structure would thus be a parent substrate 1, an adhesion-mediating layer 2, a first interlayer 3, a second interlayer 5, a diamond-like carbon layer 4, a first interlayer 3 and a diamond-like carbon layer 4. The structure may alternatively comprise a parent substrate 1, an adhesion-mediating layer 2, two first interlayers 3, a diamond-like carbon layer 4, a first interlayer 3 and a diamond-like carbon layer 4; or a parent substrate 1, and adhesion mediating layer 2, a first interlayer 3, a second interlayer 5, a first interlayer 3, a diamond-like carbon layer 4, a first interlayer 3 and a diamond-like carbon layer 4. The aforementioned illustrative structures are not comprehensive, and other structure configurations may be employed within the scope of the invention to achieve the objectives of excellent resistance to abrasion, chemical attack and impact.

By choosing the appropriate interlayer 3, 5 and diamond-like carbon layer 4 thicknesses, criteria which are known in the art of optical coating design could be employed in each of the aforementioned embodiments of the present invention to produce quarter wavelength stacks and other "dielectric stack" coating configurations. In these dielectric stack configurations, optical interference effects could be used to produce wavelength-selective mirrors or anti-reflection films. Additionally, the reflection of light at predetermined wavelength ranges may be either minimized or maximized by choosing the appropriate thickness of at least one of the interlayers 3, 5 and diamond-like carbon layer 4.

WO 92/06843

PCT/US91/07209

-18-

Superior abrasion wear resistance and environmental durability currently unavailable with conventional optical coatings could thus be realized by the incorporation of the dielectric stack configurations into the present invention.

The method of the present invention teaches those skilled in the art how to fabricate the transparent abrasion wear resistant coated polymeric substrate product. According to the method, the first step involves chemically de-greasing the surface of the parent substrate 1. The substrate 1 is then coated with a polysiloxane polymer layer 2 (see Figure 1) by a conventional dip, flow, spray or other solution-based coating process. After the polysiloxane layer 2 is thermally cured, the coated surface of the substrate 1 is chemically cleaned. The substrate 1 is then placed into a chemical vapor deposition reactor vacuum chamber and the air evacuated from the chamber to less than approximately 5×10^{-6} Torr.

In the next step, the surface of the substrate 1 is sputter-etched with energetic ions or atoms to assist in the removal of residual hydrocarbons, as well as alkali metals and other additives which are commonly present on the surface of the substrate materials. In accordance with the invention, it has been found that the concentration of alkali metals (i.e. Na, Ca) at the surface of a substrate was significantly reduced as a function of ion sputter-etching time and that increased sputter-etching time substantially improved the adhesion of the diamond-like carbon layer 4. [See Examples 1-15] Therefore, it is concluded that the removal of alkali metals and other additives is also essential to achieve a highly adherent interface between parent substrate 1 and the diamond-like carbon layer 4.

The sputter-etching may be performed with a beam of inert gas ions, hydrogen ions or oxygen ions, a glow

WO 92/06843

PCT/US91/07209

-19-

discharge or a plasma of inert gas, hydrogen or oxygen. In the preferred embodiment form of the invention, sputter-etching is performed with a beam of energetic gas ions at an energy of at least 200 eV.

5 Following the sputter-etching step, one or more interlayers are chemically vapor deposited onto the parent substrate 1. During a first cycle any of the
10 aforementioned conventional chemical vapor deposition methods may be employed to deposit the interlayers 3,5
15 The deposition rate of each interlayer 3,5 is generally in the range of about 0.1-10 microns/hour. The total thickness of each interlayer can be in the range of about 5 Å to 10,000 Å. In the preferred embodiment form of the invention, the total thickness for each interlayer 3,5
15 is at least 10 Å, or at least 200 Å if silicon dioxide is employed.

 During the chemical vapor deposition of the interlayers 3,5 it is desirable to operate the reactor chamber at a temperature which is as low as possible. It
20 has been found that decreasing the substrate 1 temperature generally improves the adherence of the diamond-like carbon layer 4 and also eliminates any danger of heating the plastic substrate 1 to a temperature which would be within the softening range for
25 the plastic material. Therefore, in the preferred embodiment form of the invention, the temperature of the parent substrate 1 is maintained at less than 125°C during the chemical vapor deposition step(s).

 After the chemical vapor deposition of one or
30 more interlayers onto the parent substrate 1, a diamond-like carbon layer 4 is deposited onto the coated substrate. The diamond-like carbon layer 4 can be deposited by the following conventional methods; (i) direct ion beam deposition, dual ion beam deposition,
35 glow discharge, RF-plasma, DC-plasma, or microwave plasma deposition from a carbon-containing gas or a carbon-

WO 92/06843

PCT/US91/07209

-20-

containing vapor which can also be mixed with hydrogen, nitrogen-containing gases, oxygen containing gases and/or inert gas, (ii) electron beam evaporation, ion-assisted evaporation, magnetron sputtering, ion beam sputtering, or ion-assisted sputter deposition from a solid carbon target material, or (iii) combinations of (i) and (ii).

In the preferred embodiment form of the invention, the diamond-like carbon layer(s) 4 is deposited by ion beam deposition from a hydrocarbon gas or carbon vapor. The ion beam deposition may also be performed in combination with an inert gas or hydrogen.

The deposition rate of the diamond-like carbon layer 4 is generally in the range of about 0.1-10 microns/hour. The total thickness of the diamond-like carbon layer 4 is generally in the range of about 10 Å to 10 micrometers. Preferably, the thickness of the diamond-like carbon layer 4 is at least 200 Å thick.

After the deposition of the appropriate interlayers and diamond-like carbon layer(s) 4, as detailed in the aforementioned embodiments, the coated substrate product is cooled by extinguishing the deposition process and passing an inert gas over the substrate until it has reached substantially room temperature. The coated substrate product, exhibiting superior resistance to abrasion and chemical attack, is then removed from the reactor.

The examples which follow demonstrate that abrasion-resistant and highly adherent diamond-like hard carbon coatings can be applied to the surface of plastic substrates, such as optical lenses. The examples are for illustrative purposes only and are not meant to limit the scope of the claims in any way.

Example No. 1 illustrates that the invention can be used to apply adherent and abrasion-resistant diamond-like hard carbon coatings applied to polycarbonate and CR-39 plastic lenses. Example No. 1 also illustrates

WO 92/06843

PCT/US91/07209

-21-

the critical influence of the polysiloxane polymer layer thickness on the abrasion resistance of the diamond-like carbon coated substrate product. Example Nos. 2-6 illustrate the critical influence of the silicon dioxide interlayer thickness on the adhesion of the diamond-like carbon outer layer. Example Nos. 7-14 illustrate that a variety of reflected colors can be produced by including a metallic layer in the coating stack, and depositing different thicknesses of a silicon dioxide interlayer and diamond-like carbon over the metallic layer. Example No. 15 illustrates the deposition of alternating layers of silicon dioxide and diamond-like carbon over the polysiloxane polymer layer to form a quarter wavelength stack coating made of silicon dioxide and diamond-like carbon.

Table I is a summary of the Young's Modulus and Hardness of the layers used in Examples 1-15.

Table I

Young's Modulus and Hardness for typical layers used in the Examples 1-15.*

Material or Coating	Hardness (GPa)	Young's Modulus (GPa)
Polycarbonate	0.23	3.8
Polysiloxane (1)	0.73	4.7
SiO ₂ (2)	8.6	88
DLC (3)	12-21	100-170

Notes: (1) Layer formed by dip coating/thermal curing process

(2) Layer formed by Ar⁺ ion beam sputter-deposition from a quartz target.

(3) Layer formed by direct ion beam deposition from CH₄/Ar gas.

*All values determined by nanoindentation measurement.

WO 92/06843

PCT/US91/07209

-22-

EXAMPLE 1

Eight polycarbonate sunglass lenses and two CR-39[®] clear ophthalmic lenses were vapor-degreased with Freon, and then dip-coated with a polysiloxane polymer layer which was thermally cured at approximately 250°F. The polysiloxane layers on each substrate were prepared in an identical fashion, with the exception that the polysiloxane layer thickness was adjusted to be 1.3 microns for polycarbonate lens No. 1, 2.2 microns for polycarbonate lens No. 2, 3.0 microns for polycarbonate lens No. 3, 5.0 microns for polycarbonate lens No. 4, and 3 microns for CR-39[®] lens No. 5. After the curing process was complete, each lens was ultrasonically cleaned in a solvent bath of isopropyl alcohol, and then blown dry with nitrogen gas. The lenses were mounted onto a substrate holder and inserted into a vacuum coating chamber which was evacuated to approximately 4×10^{-6} Torr. The substrates were sputter-etched for 20 minutes by a beam of Ar^+ ions at an energy of 500 eV and an ion beam current of 90 mA. Next, a 600-Angstroms thick layer of silicon dioxide (SiO_2) was deposited onto the lenses by Ar^+ ion beam sputter deposition from a quartz target. The lenses were then coated with top layer of diamond-like carbon by direct ion beam deposition using an 11 cm ion beam source operated on 6 sccm of CH_4 and 3 sccm of Ar gas at a pressure of approximately 3×10^{-4} Torr. The ion energy was 50 eV and the ion beam current was 150 mA. A transparent diamond-like hard carbon layer, 800 Angstroms thick, was deposited onto each lens.

After cooling under Ar gas flow for 5 minutes, the lenses were removed from the reactor. Lenses 1A, 2A, 3A, 4A, and 5A were tested for coating adhesion by immersion in a bath of boiling salt water (5% NaCl) for 20 minutes followed by rinsing in cold water. After

WO 92/06843

PCT/US91/07209

-23-

removal of the lenses from the salt water bath, all of the coatings appeared undamaged, and did not crack, craze, or peel off the substrate.

5 Lenses 1B, 2B, 3B, 4B, and 5B were tested for abrasion resistance by NFPA 1981 Standard on Open-Circuit Self-Contained Breathing Apparatus for Fire Fighters (1987 Edition) Test Number 4-9, "Facepiece Lens Abrasion Resistance Test," using vertical weights of 4 and 12 pounds applied to #0000 steel wool. The abrasion test
10 results are summarized in Table II below.

Table II
Steel Wool Abrasion Test Results

15

Lens No.	Substrate	Polysiloxane	4-Pound	12-Pound
	Material	Thickness	Result	Result
1B	polycarbonate	1.3 microns	moderate	heavy
20 2B	polycarbonate	2.2 microns	moderate	heavy
3B	polycarbonate	3.0 microns	slight	moderate/heavy
4B	polycarbonate	5.0 microns	none	slight
5B	CR-39 [®]	3.0 microns	none	none/slight

25 Definitions of Observed Damage Results:

Heavy = Many overlapping deep scratches visible to
naked eye. Microscopically (200x), DLC
coating removed; many scratches deep into
30 substrate.

Moderate = Many isolated scratches visible to naked eye.
Microscopically (200x), DLC coating crushed
into polysiloxane layer; few deep scratches.

35

(Definitions of Observed Damage Results):

Slight = Few isolated fine scratches visible to naked eye. Microscopically (200x), "indentation scratches" observed, but DLC coating is not cracked.

None = No damage visible to the naked eye.
Microscopically, few isolated fine
"indentation scratches."

For reference, an uncoated polycarbonate lens exhibited heavy damage when abraded by the steel wool using a 4 pound vertical weight. The abrasion test results clearly demonstrated a dramatic improvement in abrasion resistance when the polysiloxane polymer layer was at least 3 microns thick.

EXAMPLE 2

An 80 mm diameter x 2 mm thick neutral gray polycarbonate sunglass lens was coated by the following procedure. After molding, the lens was vapor-degreased with Freon, then dip-coated with a polysiloxane polymer layer which was thermally cured. The polysiloxane layer was 3 microns thick. After the curing process was complete, the lens was ultrasonically cleaned in a solvent bath of isopropyl alcohol, and blown dry with nitrogen gas. The lens was then mounted onto a substrate holder and inserted into a vacuum chamber which was evacuated to about 1.4×10^{-6} Torr. The sample was sputter-etched for 3 minutes by a beam of Ar^+ ions at an energy of 500 eV and an ion beam current of 90 mA. Next, a 850-Angstroms thick layer of SiO_2 was deposited onto the lens by Ar^+ ion beam sputter deposition from a quartz target. The sample was then coated with diamond-like carbon by direct ion beam deposition from a quartz target. The sample was then coated with diamond-like

WO 92/06843

PCT/US91/07209

-25-

carbon by direct ion beam deposition using an 11 cm ion beam source operated on 6 sccm of CH_4 gas and 3 sccm of Ar gas at a pressure of 1.9×10^{-4} Torr. The ion energy was 75 eV and the ion beam current was 180 mA.

5 After cooling under Ar gas flow for 5 minutes, the lens was removed from the reactor. The coating was then tested for adhesion by immersing the sample in a bath of boiling salt water (5% NaCl) for 30 minutes. After removal of the sample from the salt water bath, the
10 coating appeared undamaged, and did not crack, craze, or peel off the substrate. A cross-hatch/tape adhesion test indicated no adhesion failure of the coating.

EXAMPLE 3

15 A neutral gray polycarbonate sunglass lens coated with a 1.5-micron thick coating of polysiloxane polymer was prepared by the procedure in Example 2. Next, the lens was inserted into a vacuum coating chamber and evacuated to a pressure of 3×10^{-7} Torr. The lens was then sputter-etched for 3 minutes by a beam of Ar^+ ions
20 at an energy of 500 eV and an ion beam current of 67 mA. Then, the vacuum coating procedure in Example 2 was repeated, except no SiO_2 coating was deposited between the polysiloxane layer and the diamond-like carbon layer. The diamond-like carbon coating cracked and spalled from
25 the substrate surface soon after removal from the vacuum coating chamber, indicating very poor adhesion.

EXAMPLE 4

30 The procedure in Example 2 was repeated, except the vacuum coating chamber was evacuated to 1.2×10^{-6} Torr, and the SiO_2 coating thickness was 200 Angstroms. After 30 minutes exposure to boiling salt water, the coating exhibited some crazing (spalling), indicating inadequate adhesion. However, the adhesion of the diamond-like carbon coating was much greater than that
35 found in Example 3.

WO 92/06843

PCT/US91/07209

-26-

EXAMPLE 5

The procedure in Example 2 was repeated, except the vacuum coating chamber was evacuated to 2.1×10^{-6} Torr, and the SiO_2 coating thickness was 550 Angstroms. After 10 minutes exposure to boiling salt water, the diamond-like carbon coating appeared undamaged, and did not crack, craze, or peel off the substrate, indicating excellent adhesion.

EXAMPLE 6

The procedure in Example 2 was repeated, except the vacuum coating chamber was evacuated to 2.5×10^{-6} Torr and the SiO_2 coating thickness was 650 Angstroms. After 30 minutes exposure to boiling salt water, the diamond-like carbon coating appeared undamaged, and did not crack, craze, or peel off the substrate, indicating excellent adhesion.

EXAMPLE 7

An 80 mm diameter x 2mm thick neutral gray polycarbonate sunglass lens was coated by the following procedure. After molding, the lens was vapor-degreased with Freon, then dip-coated with a polysiloxane polymer layer which was thermally cured. The polysiloxane layer was 3 microns thick. After the curing process was complete, the lens was ultrasonically cleaned in a solvent bath of isopropyl alcohol, and blown dry with nitrogen gas. The lens was then mounted onto a substrate holder and inserted into a vacuum chamber which was evacuated to 5×10^{-6} Torr. The substrate was sputter-etched for 4 minutes by a beam of Ar^+ ions at an energy of 500 eV and an ion beam current of 90 mA. Next, a 200-Angstroms thick layer of SiO_2 was deposited onto the lens by Ar^+ ion beam sputter deposition from a quartz target. Then, a 100-Angstroms thick layer of Cr was deposited on top of the SiO_2 layer by Ar^+ ion beam sputter deposition from a Cr metal target. Then, a 300-Angstroms thick layer of SiO_2 was ion beam sputter-deposited on top of

WO 92/06843

PCT/US91/07209

-27-

the Cr layer. Finally, a 500-Angstroms thick layer of transparent diamond-like hard carbon was deposited on top of the second SiO₂ layer by direct ion beam deposition using an 11 cm ion beam source operated on 6 sccm of CH₄ and 3 sccm of Ar gas at a pressure of 4.8×10^{-5} Torr. The ion energy was 75 eV and the ion beam current was 140 mA. The resultant lens was coated with an abrasion-resistant diamond-like carbon coating and exhibited a violet-blue reflected color.

10

EXAMPLE 8

An 80 mm diameter x 2 mm thick neutral gray sunglass lens was dip-coated with 3 microns of polysiloxane polymer, cleaned, and inserted into a vacuum chamber as described in Example 7. The vacuum chamber was then evacuated to a pressure of 4.5×10^{-7} Torr. The substrate was sputter-etched for 4 minutes by a beam of Ar⁺ ions at an energy of 500 eV and an ion beam current of 90 mA. Next, a 200-Angstroms thick layer of SiO₂ was deposited onto the lens by Ar⁺ ion beam sputter deposition from a quartz target. Then, a 100-Angstroms thick layer of Si was deposited on top of the SiO₂ layer by Ar⁺ ion beam sputter deposition from a Si target. Then, a 300-Angstrom thick layer of SiO₂ was ion beam sputter-deposited on top of the Si layer. Finally, a 480-Angstroms thick layer of transparent diamond-like hard carbon was deposited on top of the second SiO₂ layer by direct ion beam deposition using the conditions described in Example 7. The resultant lens was coated with an abrasion-resistant diamond-like carbon coating and exhibited a pink-gold reflected color.

30

EXAMPLE 9

An 80 mm diameter x 2 mm thick neutral gray sunglass lens was dip-coated with 3 microns of polysiloxane polymer, cleaned, and inserted into a vacuum chamber as described in Example 7. The vacuum chamber was then evacuated to a pressure of 2.0×10^{-6} Torr. The

35

WO 92/06843

PCT/US91/07209

-28-

substrate was sputter-etched for 4 minutes by a beam of Ar^+ ions at an energy of 500 eV and an ion beam current of 90 mA. Next, a 500-Angstroms thick layer of SiO_2 was deposited onto the lens by Ar^+ ion beam sputter deposition from a quartz target. Then, a 100-Angstroms thick layer of Si was deposited on top of the SiO_2 layer by Ar^+ ion beam sputter deposition from a Si target. Finally, a 480-Angstroms thick layer of transparent diamond-like hard carbon was deposited on top of the Si layer by direct ion beam deposition using the conditions described in Example 7. The resultant lens was coated with an abrasion-resistant diamond-like carbon coating and exhibited a gold reflected color.

EXAMPLE 10

An 80 mm diameter x 2 mm thick neutral gray sunglass lens was dip-coated with 3 microns of polysiloxane polymer, cleaned, and inserted into a vacuum chamber as described in Example 7. The vacuum chamber was then evacuated to a pressure of 3.0×10^{-6} Torr. The substrate was sputter-etched for 4 minutes by a beam of Ar^+ ions at an energy of 500 eV and an ion beam current of 90 mA. Next, a 200 Angstroms thick layer of SiO_2 was deposited onto the lens by Ar^+ ion beam sputter deposition from a quartz target. Then, a 100-Angstroms thick layer of Mo was deposited on top of the SiO_2 layer by Ar^+ ion beam sputter deposition from a Mo target. Then, a 300-Angstroms thick layer of SiO_2 was ion beam sputter-deposited on top of the Mo layer. Finally, a 640-Angstroms thick layer of transparent diamond-like hard carbon was deposited on top of the second SiO_2 layer by direct ion beam deposition using the conditions described in Example 7. The resultant lens was coated with an abrasion-resistant diamond-like coating and exhibited a blue reflected color.

EXAMPLE 11

A 2.5" wide x 6" long x 2 mm thick 6-base

WO 92/06843

PCT/US91/07209

-29-

cylinder violet polycarbonate sunglass lens was dip-coated with 5 microns of polysiloxane polymer, cleaned, and inserted into a vacuum chamber as described in Example 2. Then, the vacuum chamber was evacuated to a pressure of 2×10^{-6} Torr. The substrate was sputter-etched for 4 minutes by a beam of Ar^+ ions at an energy of 500 eV and an ion beam current of 90 mA. Next, a 860-Angstroms thick layer of SiO_2 was deposited onto the lens by Ar^+ ion beam sputter deposition from a quartz target. Then, a 100-Angstroms thick layer of Ge was deposited on top of the SiO_2 layer by Ar^+ ion beam sputter deposition from a Ge target. Then, a 700-Angstroms thick layer of transparent diamond-like hard carbon was deposited on top of the Ge layer by direct ion beam deposition using the conditions described in Example 2.

The resultant lens was coated with an abrasion-resistant diamond-like carbon coating which exhibited a gold reflected color. The diamond-like carbon coating exhibited excellent adhesion after tensile and compression flexing of the lens, and was not damaged after exposure to 30 minutes of boiling salt water.

EXAMPLE 12

A 2.5" wide x 6" long x 2 mm thick 6-base cylinder violet polycarbonate sunglass lens was dip-coated with 5 microns of polysiloxane polymer, cleaned, and inserted into a vacuum chamber as described in Example 2. The vacuum chamber was then evacuated to a pressure of 2×10^{-6} Torr. The substrate was sputter-etched for 4 minutes by a beam of Ar^+ ions at an energy of 500 eV and an ion beam current of 90 mA. Next, a 860-Angstroms thick layer of SiO_2 was deposited onto the lens by Ar^+ ion beam sputter deposition from a quartz target. Then, a 100-Angstroms thick layer of Ge was deposited on top of the SiO_2 layer by Ar^+ ion beam sputter deposition from a Ge target. Next, a 500-Angstroms thick layer of SiO_2 was deposited on top of the Ge layer using the

WO 92/06843

PCT/US91/07209

-30-

method described above. Finally, a 500-Angstroms thick layer of transparent diamond-like hard carbon was deposited on top of the second SiO₂ layer by direct ion beam deposition using the conditions described in Example

5 2.

The resultant lens was coated with an abrasion resistant diamond-like carbon coating which exhibited a purple reflected color. The diamond-like carbon coating exhibited excellent adhesion after tensile and
10 compression flexing of the lens, and was not damaged after exposure to 30 minutes of boiling salt water.

EXAMPLE 13

A 2.5" wide x 6" long x 2 mm thick 6-base cylinder violet polycarbonate sunglass lens was dip-
15 coated with 5 microns of polysiloxane polymer, cleaned, and inserted into a vacuum chamber as described in Example 2. The vacuum chamber was then evacuated to a pressure of 5×10^{-6} Torr. The substrate was sputter-
20 etched for 4 minutes by a beam of Ar⁺ ions at an energy of 500 eV and an ion beam current of 90 mA. Next, a 430-Angstroms thick layer of SiO₂ was deposited onto the lens by Ar⁺ ion beam sputter deposition from a quartz target. Then, a 100 Angstroms thick layer of Ge was deposited on
25 top of the SiO₂ layer by Ar⁺ ion beam sputter deposition from a Ge target. Next, a 400-Angstroms thick layer of SiO₂ was deposited on top of the Ge layer using the method described above. Then, a 400-Angstroms thick first layer of transparent diamond-like hard carbon was deposited on top of second SiO₂ layer using the
30 conditions described in Example 2. Next, a third 400-Angstroms thick layer of SiO₂ was deposited on top of the first diamond-like carbon layer using the method described above. Finally, a second 400-Angstroms thick layer of transparent diamond-like carbon was deposited on
35 top of the third SiO₂ layer using the conditions described in Example 2.

WO 92/06843

PCT/US91/07209

-31-

The resultant lens was coated with an abrasion-resistant diamond-like carbon coating which exhibited a silver-blue reflected color. The diamond-like carbon coating exhibited excellent adhesion after tensile and compression flexing of the lens, and was not damaged after exposure to 30 minutes of boiling salt water.

EXAMPLE 14

A 2.5" wide x 6" long x 2 mm thick 6-base cylinder violet polycarbonate sunglass lens was dip-coated with 5 microns of polysiloxane polymer, cleaned, and inserted into a vacuum chamber as described in Example 2. The vacuum chamber was then evacuated to a pressure of 2×10^{-6} Torr. The substrate was sputter-etched for 4 minutes by a beam of Ar^+ ions at an energy of 500 eV and an ion beam current of 90 mA. Next, a 425-Angstroms thick layer of SiO_2 was deposited onto the lens by Ar^+ ion beam sputter deposition from a quartz target. Then, a 100-Angstroms thick layer of Ge was deposited on top of the SiO_2 layer by Ar^+ ion beam sputter deposition from a Ge target. Next, a 440-Angstroms thick second layer of SiO_2 was deposited on top of the Ge layer using the method described above. Then, a 440-Angstroms thick first layer of transparent diamond-like carbon was deposited using the conditions described in Example 2. Next, a 440-Angstroms thick third layer of SiO_2 was deposited on top of the diamond-like carbon layer, using the method described above. Then, a 440-Angstroms thick second layer of transparent diamond-like carbon was deposited using the conditions described in Example 2. Then, a 440-Angstroms thick fourth layer of SiO_2 was deposited as described above. Last, a 440-Angstroms thick third layer of transparent diamond-like carbon was deposited as the final layer of the stack, using the conditions described in Example 2.

The resultant lens was coated with an abrasion-resistant diamond-like carbon coating which exhibited a

WO 92/06843

PCT/US91/07209

-32-

red-pink reflected color. The diamond-like carbon coating exhibited excellent adhesion after tensile and compression flexing of the lens, and was not damaged after exposure to 30 minutes of boiling salt water.

5

Table III

Summary of results of polycarbonate
lenses coated in Examples 8-14

Ex.	Polysiloxane Thickness	Stack Layer/ Coating Structure	Reflected Color
7	3 microns	200 Å SiO ₂ /100 Å Cr/ 300 Å SiO ₂ /500 Å DLC	violet blue
8	3 microns	200 Å SiO ₂ /100 Å Si/ 300 Å SiO ₂ /480 Å DLC	pink/gold
9	3 microns	500 Å SiO ₂ /100 Å Si/600 Å DLC	gold
10	3 microns	200 Å SiO ₂ /100 Å Mo/ 300 Å SiO ₂ /640 Å DLC	blue
11	5 microns	860 Å SiO ₂ /100 Å Ge/700 Å DLC	gold
12	5 microns	860 Å SiO ₂ /100 Å Ge/ 500 Å SiO ₂ /500 Å DLC	purple
13	5 microns	430 Å SiO ₂ /100 Å Ge/400 Å SiO ₂ / 400 Å DLC/400 Å SiO ₂ /400 Å DLC	silver-blue
14	5 microns	425 Å SiO ₂ /100 Å Ge/200 Å SiO ₂ / 440 Å DLC/440 Å SiO ₂ /440 Å SiO ₂ / 440 Å DLC	red-pink

35

WO 92/06843

PCT/US91/07209

-33-

EXAMPLE 15

An adherent, abrasion-resistant quarter-wavelength stack reflecting coating was formed on polycarbonate lenses. The layer thicknesses were chosen to maximize reflectance at 550 nanometers. The refractive index of the deposited SiO_2 layer was 1.45, and the refractive index of the deposited diamond-like carbon layer was 2.0. The coating was formed as follows.

An 80 mm diameter x 2 mm thick neutral gray polycarbonate sunglass lens and an 80 mm diameter x 2 mm thick clear polycarbonate lens were dip-coated with 3 microns of polysiloxane polymer, cleaned, and inserted into a vacuum chamber as described in Example 2. The chamber was evacuated to a pressure of 6.0×10^{-7} Torr. The substrates were sputter-etched for 3 minutes by a beam of Ar^+ ions at an energy of 200 eV and an ion beam current of 40 mA. Next, a 945-Angstroms thick layer of SiO_2 was deposited onto the lenses by Ar^+ ion beam sputter deposition from a quartz target. Then, a 685-Angstroms thick layer of transparent diamond-like hard carbon was deposited on top of the first SiO_2 layer, using the conditions described in Example 2. Next, a second 945-Angstroms thick layer of SiO_2 was deposited as described above. Finally, a second 685-Angstroms thick layer of transparent diamond-like hard carbon was deposited on top of the second SiO_2 layer using the conditions described in Example 2. The coating was very adherent, had a high reflectance to visible light (550 nm) and exhibited a pale gold-blue reflected color on the neutral gray lens.

From the foregoing description, one of ordinary skill in the art can easily ascertain that the present invention provides a novel method for producing a substantially optically transparent multilayer composite structure. A highly important technical advantage of the invention is that superior abrasion wear resistance is

WO 92/06843

PCT/US91/07209

-34-

achieved by use of a multilayer transparent structure comprised of a parent substrate, one or more interlayers and a diamond-like carbon outer layer.

5 Without departing from the spirit and scope of this invention, one of ordinary skill can make various changes and modifications to the invention to adapt it to various usages and conditions. As such, these changes and modifications are properly, equitably, and intended to be, within the full range of equivalents of the
10 following claims.

WO 92/06843

PCT/US91/07209

-35-

WHAT IS CLAIMED IS:

1. A coated substrate product comprised of a substantially optically transparent polymeric substrate and a first composite layer, said first composite layer comprising a substantially optically transparent
5 adhesion-mediating layer bonded to and disposed towards said substrate of a polysiloxane polymer having a high elasticity and capable of forming a strong chemical bond
10 to said polymeric substrate, a chemically vapor deposited first interlayer bonded to and disposed immediately adjacent to said adhesion-mediating layer of a substantially optically transparent material devoid of alkali metal atoms and fluorine and capable of forming a
15 strong chemical bond to said adhesion-mediating layer and diamond-like carbon, and a chemically vapor deposited first layer of substantially optically transparent diamond-like carbon bonded to and disposed immediately adjacent to said first interlayer and away from said
20 substrate.

2. The product of Claim 1 wherein said adhesion-mediating layer is at least 3 microns thick.

3. The product of Claim 1 wherein said first diamond-like carbon layer is at least 200 Å thick.

25 4. The product of Claim 1 wherein said first interlayer comprises a substantially optically transparent material selected from the group consisting of silicon nitride, titanium nitride, tantalum nitride, tungsten nitride, molybdenum nitride, hafnium nitride, zirconium nitride, boron nitride, silicon oxide, silicon
30 dioxide, yttrium oxide, germanium oxide, hafnium oxide, tantalum oxide, titanium oxide, zirconium oxide, tungsten oxide, molybdenum oxide, boron oxide, silicon carbide, germanium carbide and mixtures thereof.

35 5. The product of Claim 4 wherein said first interlayer is at least 10 Å thick.

WO 92/06843

PCT/US91/07209

-36-

6. The product of Claim 1 wherein said first interlayer comprises silicon dioxide.

7. The product of Claim 6 wherein said first interlayer is at least 200 Å thick.

5 8. The product of Claim 1 wherein the thickness of at least one of said first interlayer and said first diamond-like carbon layer is selected to minimize the reflection of light at predetermined wavelengths.

10 9. The product of Claim 1 wherein the thickness of at least one of said first interlayer and said first diamond-like carbon layer is selected to maximize the reflection of light at predetermined wavelengths.

15 10. The product of Claim 1 wherein the thickness of said first interlayer and said first diamond-like carbon layer corresponds to integer multiples of quarter wavelength optical thickness at predetermined wavelengths.

20 11. The product of Claim 1 wherein the compressive stress of said first interlayer is less than said first diamond-like carbon layer and greater than said adhesion-mediating layer.

12. The product of Claim 1 wherein said first interlayer exhibits a tensile stress and said first diamond-like carbon layer exhibits a compressive stress.

25 13. The product of Claim 1 including at least a second composite layer bonded to and disposed immediately adjacent to said first composite layer, said second composite layer comprising a second interlayer bonded to and disposed immediately adjacent to said first diamond-like carbon layer and away from said substrate and a
30 second diamond-like carbon layer bonded to and disposed immediately adjacent to said second interlayer and away from said substrate.

35 14. The product of Claim 13 wherein said second interlayer comprises a substantially optically transparent material selected from the group consisting of silicon nitride, titanium nitride, tantalum nitride, tungsten

WO 92/06843

PCT/US91/07209

-37-

nitride, molybdenum nitride, hafnium nitride, zirconium nitride, boron nitride, silicon oxide, silicon dioxide, yttrium oxide, germanium oxide, tungsten oxide, molybdenum oxide, boron oxide, hafnium oxide, tantalum oxide, titanium oxide, zirconium oxide, silicon carbide, germanium carbide and mixtures thereof.

15. The product of Claim 14 wherein the thickness of said second interlayer is at least 10 Å thick.

16. The product of Claim 13 wherein said second interlayer comprises silicon dioxide.

17. The product of Claim 16 wherein said second interlayer is at least 200 Å thick.

18. The product of Claim 13 wherein the thickness of said second diamond-like carbon layer is at least 200 Å thick.

19. The product of Claim 13 wherein the thickness of at least one of said first interlayer, said first diamond-like carbon layer, said second interlayer and said second diamond-like carbon layer is selected to minimize the reflection of light at predetermined wavelengths.

20. The product of Claim 13 wherein the thickness of at least one of said first interlayer, said first diamond-like carbon layer, said second interlayer and said second diamond-like carbon layer is selected to maximize the reflection of light at predetermined wavelengths.

21. The product of Claim 13 wherein the thickness of said first interlayer, said first diamond-like carbon layer, said second interlayer and said second diamond-like carbon layer corresponds to integer multiples of quarter wavelength optical thickness at predetermined wavelengths.

22. The product of Claim 13 wherein the thickness of said first diamond-like carbon layer, said second interlayer and said second diamond-like carbon layer corresponds to integer multiples of quarter wavelength optical thickness at predetermined wavelengths.

23. The product of Claim 13 wherein the

WO 92/06843

PCT/US91/07209

-38-

compressive stress of said second interlayer is less than said second diamond-like carbon layer.

24. The product of Claim 13 wherein said second interlayer exhibits a tensile stress and said first
5 diamond-like carbon layer and said second diamond-like carbon layer exhibit a compressive stress.

25. The product of Claim 1 wherein said first composite layer includes a chemically vapor deposited third interlayer bonded to and disposed between said first
10 interlayer and said first diamond-like carbon layer of a substantially optically transparent material capable of forming a strong chemical bond to said first interlayer and said first diamond-like carbon layer.

26. The product of Claim 25 wherein said first
15 interlayer comprises a substantially optically transparent material selected from the group consisting of silicon nitride, titanium nitride, tantalum nitride, tungsten nitride, molybdenum nitride, hafnium nitride, zirconium nitride, boron nitride, silicon dioxide, silicon oxide, yttrium oxide, germanium oxide, tungsten oxide, molybdenum
20 oxide, boron oxide, hafnium oxide, silicon oxide, silicon dioxide, tantalum oxide, titanium oxide, zirconium oxide, silicon carbide, germanium carbide, aluminum oxide, cerium oxide, tin oxide, thorium oxide, lithium oxide, sodium
25 oxide, potassium oxide, rubidium oxide, cesium oxide, francium oxide, beryllium oxide, magnesium oxide, calcium oxide, strontium oxide, barium oxide, radium oxide, barium fluoride, cerium fluoride, magnesium fluoride, thorium fluoride, calcium fluoride, neodymium fluoride, lead
30 fluoride, sodium fluoride, lithium fluoride, zinc selenide, zinc sulfide and mixtures thereof.

27. The product of Claim 25 wherein said third interlayer comprises a substantially optically transparent material selected from the group consisting of silicon
35 nitride, titanium nitride, tantalum nitride, hafnium nitride, tungsten nitride, molybdenum nitride, zirconium

WO 92/06843

PCT/US91/07209

-39-

nitride, boron nitride, silicon dioxide, silicon oxide, yttrium oxide, germanium oxide, hafnium oxide, tungsten oxide, molybdenum oxide, boron oxide, tantalum oxide, titanium oxide, zirconium oxide, silicon carbide, germanium carbide, and mixtures thereof.

28. The product of Claim 27 wherein said third interlayer is at least 10 Å thick.

29 The product of Claim 25 wherein said third interlayer comprises silicon dioxide.

30. The product of Claim 29 wherein the thickness of said third interlayer is at least 200 Å.

31. The product of Claim 25 wherein said third interlayer comprises a substantially optically transparent metallic material capable of reflecting visible light selected from the group consisting of silicon, germanium, hafnium, molybdenum, tungsten, yttrium, tantalum, titanium and zirconium.

32. The product of Claim 31 wherein said third interlayer is at least 25 Å thick.

33. The product of Claim 25 wherein said third interlayer comprises a substantially optically transparent metallic material capable of reflecting visible light selected from the group consisting of vanadium, niobium, chromium, manganese, rhenium, technetium, iron, cobalt, iridium, rhodium, nickel, palladium, platinum, copper, silver, gold, zinc, ruthenium, indium, aluminum, tin, osmium, thallium, lead, antimony, bismuth and polonium.

34. The product of Claim 33 wherein said third interlayer is at least 25 Å thick.

35. The product of Claim 25 wherein the thickness of at least one of said first interlayer, said third interlayer and said first diamond-like carbon layer is selected to minimize the reflection of light at predetermined wavelengths.

36. The product of Claim 25 wherein the thickness of at least one of said first interlayer, said third

WO 92/06843

PCT/US91/07209

-40-

interlayer and said first diamond-like carbon layer is selected to maximize the reflection of light at predetermined wavelengths.

37. The product of Claim 25 wherein the thickness
5 of said first interlayer, said third interlayer and said first diamond-like carbon layer corresponds to integer multiples of quarter wavelength optical thickness at predetermined wavelengths.

38. The product of Claim 25 wherein the thickness
10 of said third interlayer and said first diamond-like carbon layer corresponds to integer multiples of quarter wavelength optical thickness at predetermined wavelengths.

39. The product of Claim 25 wherein the
compressive stress of said third interlayer is less than
15 said first diamond-like carbon layer and greater than said adhesion-mediating layer.

40. The product of Claim 25 wherein said third
interlayer exhibits a tensile stress and said first
diamond-like carbon layer exhibits a compressive stress.

41. The product of Claim 25 including a fourth
20 interlayer disposed between said third interlayer and said first diamond-like carbon layer of a substantially optically transparent material devoid of alkali metal atoms and fluorine and capable of forming a strong
25 chemical bond with said third interlayer and said first diamond-like carbon layer.

42. The product of Claim 41 wherein said fourth
interlayer comprises a substantially optically transparent
material selected from the group consisting of silicon
30 nitride, titanium nitride, tantalum nitride, tungsten nitride, molybdenum nitride, hafnium nitride, zirconium nitride, boron nitride, silicon dioxide, silicon oxide, yttrium oxide, germanium oxide, hafnium oxide, tantalum oxide, tungsten oxide, molybdenum oxide, boron oxide,
35 titanium oxide, zirconium oxide, silicon carbide, germanium carbide and mixtures thereof.

WO 92/06843

PCT/US91/07209

-41-

43. The product of Claim 42 wherein said fourth interlayer is at least 10 Å thick.

44. The product of Claim 41 wherein said fourth interlayer comprises silicon dioxide.

5 45. The product of Claim 44 wherein the thickness of said fourth interlayer is at least 200 Å.

46. The product of Claim 41 wherein the thickness of at least one of said first interlayer, said third interlayer, said fourth interlayer and said first diamond-like carbon layer is selected to minimize the reflection of light at predetermined wavelengths.

47. The product of Claim 41 wherein the thickness of at least one of said first interlayer, said third interlayer, said fourth interlayer and said first diamond-like carbon layer is selected to maximize the reflection of light at predetermined wavelengths.

48. The product of Claim 41 wherein the thickness of said first interlayer, said third interlayer, said fourth interlayer and said first diamond-like carbon layer corresponds to integer multiples of quarter wavelength optical thickness at predetermined wavelengths.

49. The product of Claim 41 wherein the thickness of said third interlayer, said fourth interlayer and said first diamond-like carbon layer corresponds to integer multiples of quarter wavelength optical thickness at predetermined wavelengths.

50. The product of Claim 41 wherein the compressive stress of said fourth interlayer is less than said first diamond-like carbon layer and greater than said adhesion-mediating layer.

51. The product of Claim 41 wherein said fourth interlayer exhibits a tensile stress and said first diamond-like carbon layer exhibits a compressive stress.

52. The product of Claim 25 including at least one said second composite layer bonded to and disposed immediately adjacent to said first composite layer.

WO 92/06843

PCT/US91/07209

-42-

53. The product of Claim 52 wherein the thickness of at least one of said first interlayer, said third interlayer, said first diamond-like carbon layer, said second interlayer and said second diamond-like carbon layer is selected to minimize the reflection of light at predetermined wavelengths.

54. The product of Claim 52 wherein the thickness of at least one of said first interlayer, said third interlayer, said first diamond-like carbon layer, said second interlayer and said second diamond-like carbon layer is selected to maximize the reflection of light at predetermined wavelengths.

55. The product of Claim 52 wherein the thickness of said first interlayer, said third interlayer, said first diamond-like carbon layer, said second interlayer and said second diamond-like carbon layer corresponds to integer multiples of quarter wavelength optical thickness at predetermined wavelengths.

56. The product of Claim 52 wherein the thickness of said third interlayer, said first diamond-like carbon layer, said second interlayer and said second diamond-like carbon layer corresponds to integer multiples of quarter wavelength optical thickness at predetermined wavelengths.

57. The product of Claim 41 including at least one said second composite layer bonded to and disposed immediately adjacent to said first composite layer.

58. The product of Claim 57 wherein the thickness of at least one of said first interlayer, said third interlayer, said fourth interlayer, said first diamond-like carbon layer, said second interlayer and said second diamond-like carbon layer is selected to minimize the reflection of light at predetermined wavelengths.

59. The product of Claim 57 wherein the thickness of at least one of said first interlayer, said third interlayer, said fourth interlayer, said first diamond-like carbon layer, said second interlayer and said second

WO 92/06843

PCT/US91/07209

-43-

diamond-like carbon layer is selected to maximize the reflection of light at predetermined wavelengths.

60. The product of Claim 57 wherein the thickness of said first interlayer, said third interlayer, said
5 fourth interlayer, said first diamond-like carbon layer, said second interlayer and said second diamond-like carbon layer corresponds to integer multiples of quarter wavelength optical thickness at predetermined wavelengths.

61. The product of Claim 57 wherein the thickness
10 of said third interlayer, said fourth interlayer, said first diamond-like carbon layer, said second interlayer and said second diamond-like carbon layer corresponds to integer multiples of quarter wavelength optical thickness at predetermined wavelengths.

15 62. A chemical vapor deposition method for producing an abrasion wear resistant coated polymeric substrate product comprising: chemically degreasing the surface of a polymeric parent substrate; coating a substantially optically transparent polysiloxane polymer
20 layer onto said parent substrate to a thickness of at least 3 microns; thermally curing said polysiloxane polymer coating; chemically cleaning the coated surface of said substrate; placing said substrate into a chemical vapor deposition reactor vacuum chamber and
25 evacuating the air from said chamber to less than an approximately 5×10^{-6} Torr; sputter-etching the surface of said substrate with energetic gas ions at an energy of at least 200 eV to remove traces of residual hydrocarbon and to preferentially reduce the concentration of alkali
30 metal atoms and alkali metal oxides at the substrate surface; chemically vapor depositing during a first cycle a substantially optically transparent first interlayer capable of forming a strong chemical bond to said substrate and diamond-like carbon onto to said substrate;
35 chemically vapor depositing during said first cycle a substantially optically transparent diamond-like carbon

WO 92/06843

PCT/US91/07209

-44-

layer having a thickness of at least 200 Å onto said coated substrate; cooling said coated substrate by extinguishing said deposition process and passing an inert gas over said substrate until the temperature of said substrate has reached substantially room temperature during said cool down step; recovering a coated substrate product exhibiting superior resistance to abrasion and chemical attack.

63. The method of Claim 62 wherein the polysiloxane polymer coating step comprises a dip coating process.

64. The method of Claim 62 wherein the polysiloxane polymer coating step comprises a flow coating process.

65. The method of Claim 62 wherein the polysiloxane polymer coating step comprises a spray coating process.

66. The method of Claim 62 wherein the temperature of said parent substrate is maintained at less than 125°C during said chemical vapor deposition steps.

67. The method of Claim 62 wherein the thickness of said diamond-like carbon layer corresponds to integer multiples of quarter wavelength optical thickness at predetermined wavelengths.

68. The method of Claim 62 wherein the thickness of said first interlayer and said diamond-like carbon layer corresponds to integer multiples of quarter wavelength optical thickness at predetermined wavelengths.

69. The method of Claim 62 wherein the compressive stress of said first interlayer is less than said diamond-like carbon layer and greater than said adhesion-mediating layer.

70. The method of Claim 62 wherein said first interlayer exhibits a tensile stress and said diamond-like carbon layer exhibits a compressive stress.

71. The method of Claim 62 wherein at least a

WO 92/06843

PCT/US91/07209

-45-

second cycle is used to chemically vapor deposit at least a second interlayer and a second said diamond-like carbon layer onto said substrate.

72. The method of Claim 71 wherein the
5 compressive stress of said first interlayer and said second interlayer is less than said diamond-like carbon layer and greater than said adhesion-mediating layer.

73. The method of Claim 71 wherein said first
10 interlayer said second interlayer exhibit a tensile stress and said diamond-like carbon layer exhibits a compressive stress.

74. The method of Claim 71 wherein the deposition
15 rate for said first interlayer, said second interlayer and said diamond-like carbon layer is generally in the range of about 0.1-10 microns/hour.

75. The method of Claim 62 wherein a third
20 interlayer is chemically vapor deposited immediately adjacent to said first interlayer and away from said substrate of a substantially optically transparent material capable of forming a strong chemical bond to said first interlayer and a strong chemical bond to diamond-like carbon.

76. The method of Claim 75 wherein said diamond-
25 like carbon layer is chemically vapor deposited immediately adjacent to said second interlayer and away from said substrate.

77. The method of Claim 75 wherein the deposition
30 rate for said third interlayer is generally in the range of about 0.1-10 micron/hour.

78. The method of Claim 76 wherein the thickness
of said third interlayer and said diamond-like carbon layer corresponds to integer multiples of quarter wavelength optical thickness at predetermined wavelengths.

79. The method of Claim 76 wherein the thickness
35 of said first interlayer, said third interlayer and said diamond-like carbon layer corresponds to integer multiples

WO 92/06843

PCT/US91/07209

-46-

of quarter wavelength optical thickness at predetermined wavelengths.

80. The method of Claim 75 wherein the compressive stress of said third interlayer is less than
5 said diamond-like carbon layer and greater than said adhesion-mediating layer.

81. The method of Claim 75 wherein said third interlayer exhibits a tensile stress and said diamond-like carbon layer exhibits a compressive stress.

10 82. The method of Claim 75 wherein a second cycle is used to chemically vapor deposit at least a second said first interlayer and a second said diamond-like carbon layer onto said coated substrate.

WO 92/06843

PCT/US91/07209

47

AMENDED CLAIMS

[received by the International Bureau on 21 February 1992 (21.02.92);
original claims 1,6,16,29,44,52 and 57 amended;
other claims unchanged (12 pages)]

1. A coated substrate product comprised of a substantially optically transparent polymeric substrate and a first composite layer, said first composite layer
5 comprising a substantially optically transparent adhesion-mediating layer at least 3 microns thick bonded to and disposed towards said substrate of a polysiloxane polymer having a high elasticity and capable of forming a strong chemical bond to said polymeric substrate, a
10 chemically vapor deposited first interlayer bonded to and disposed immediately adjacent to said adhesion-mediating layer of a substantially optically transparent material devoid of alkali metal atoms and fluorine, and a
15 chemically vapor deposited first layer of substantially optically transparent diamond-like carbon bonded to and disposed immediately adjacent to said first interlayer and away from said substrate, said first interlayer being capable of forming a strong chemical bond to said
adhesion-mediating layer and diamond-like carbon.
- 20 2. The product of Claim 1 wherein said adhesion-mediating layer is at least 3 microns thick.
3. The product of Claim 1 wherein said first diamond-like carbon layer is at least 200 Å thick.
4. The product of Claim 1 wherein said first
25 interlayer comprises a substantially optically transparent material selected from the group consisting of silicon nitride, titanium nitride, tantalum nitride, tungsten nitride, molybdenum nitride, hafnium nitride, zirconium nitride, boron nitride, silicon oxide, silicon
30 dioxide, yttrium oxide, germanium oxide, hafnium oxide, tantalum oxide, titanium oxide, zirconium oxide, tungsten oxide, molybdenum oxide, boron oxide, silicon carbide, germanium carbide and mixtures thereof.
5. The product of Claim 4 wherein said first
35 interlayer is at least 10 Å thick.
6. The product of Claim 1 wherein said first

WO 92/06843

PCT/US91/07209

-48-

interlayer comprises silicon dioxide at least 200 Å thick.

7. The product of Claim 6 wherein said first interlayer is at least 200 Å thick.

8. The product of Claim 1 wherein the thickness
5 of at least one of said first interlayer and said first diamond-like carbon layer is selected to minimize the reflection of light at predetermined wavelengths.

9. The product of Claim 1 wherein the thickness
10 of at least one of said first interlayer and said first diamond-like carbon layer is selected to maximize the reflection of light at predetermined wavelengths.

10. The product of Claim 1 wherein the thickness
15 of said first interlayer and said first diamond-like carbon layer corresponds to integer multiples of quarter wavelength optical thickness at predetermined wavelengths.

11. The product of Claim 1 wherein the compressive stress of said first interlayer is less than said first diamond-like carbon layer and greater than said adhesion-mediating layer.

12. The product of Claim 1 wherein said first
20 interlayer exhibits a tensile stress and said first diamond-like carbon layer exhibits a compressive stress.

13. The product of Claim 1 including at least a second composite layer bonded to and disposed immediately
25 adjacent to said first composite layer, said second composite layer comprising a second interlayer bonded to and disposed immediately adjacent to said first diamond-like carbon layer and away from said substrate and a second diamond-like carbon layer bonded to and disposed
30 immediately adjacent to said second interlayer and away from said substrate.

14. The product of Claim 13 wherein said second interlayer comprises a substantially optically transparent material selected from the group consisting of silicon
35 nitride, titanium nitride, tantalum nitride, tungsten nitride, molybdenum nitride, hafnium nitride, zirconium

WO 92/06843

-49-

PCT/US91/07209

nitride, boron nitride, silicon oxide, silicon dioxide, yttrium oxide, germanium oxide, tungsten oxide, molybdenum oxide, boron oxide, hafnium oxide, tantalum oxide, titanium oxide, zirconium oxide, silicon carbide, germanium carbide and mixtures thereof.

15 15. The product of Claim 14 wherein the thickness of said second interlayer is at least 10 Å thick.

16. The product of Claim 13 wherein said second interlayer comprises silicon dioxide at least 200 Å thick.

10 17. The product of Claim 16 wherein said second interlayer is at least 200 Å thick.

18. The product of Claim 13 wherein the thickness of said second diamond-like carbon layer is at least 200 Å thick.

15 19. The product of Claim 13 wherein the thickness of at least one of said first interlayer, said first diamond-like carbon layer, said second interlayer and said second diamond-like carbon layer is selected to minimize the reflection of light at predetermined wavelengths.

20 20. The product of Claim 13 wherein the thickness of at least one of said first interlayer, said first diamond-like carbon layer, said second interlayer and said second diamond-like carbon layer is selected to maximize the reflection of light at predetermined wavelengths.

25 21. The product of Claim 13 wherein the thickness of said first interlayer, said first diamond-like carbon layer, said second interlayer and said second diamond-like carbon layer corresponds to integer multiples of quarter wavelength optical thickness at predetermined wavelengths.

30 22. The product of Claim 13 wherein the thickness of said first diamond-like carbon layer, said second interlayer and said second diamond-like carbon layer corresponds to integer multiples of quarter wavelength optical thickness at predetermined wavelengths.

35 23. The product of Claim 13 wherein the compressive stress of said second interlayer is less than

WO 92/06843

PCT/US91/07209

-50-

said second diamond-like carbon layer.

24. The product of Claim 13 wherein said second interlayer exhibits a tensile stress and said first diamond-like carbon layer and said second diamond-like carbon layer exhibit a compressive stress.

25. The product of Claim 1 wherein said first composite layer includes a chemically vapor deposited third interlayer bonded to and disposed between said first interlayer and said first diamond-like carbon layer of a substantially optically transparent material capable of forming a strong chemical bond to said first interlayer and said first diamond-like carbon layer.

26. The product of Claim 25 wherein said first interlayer comprises a substantially optically transparent material selected from the group consisting of silicon nitride, titanium nitride, tantalum nitride, tungsten nitride, molybdenum nitride, hafnium nitride, zirconium nitride, boron nitride, silicon dioxide, silicon oxide, yttrium oxide, germanium oxide, tungsten oxide, molybdenum oxide, boron oxide, hafnium oxide, silicon oxide, silicon dioxide, tantalum oxide, titanium oxide, zirconium oxide, silicon carbide, germanium carbide, aluminum oxide, cerium oxide, tin oxide, thorium oxide, lithium oxide, sodium oxide, potassium oxide, rubidium oxide, cesium oxide, francium oxide, beryllium oxide, magnesium oxide, calcium oxide, strontium oxide, barium oxide, radium oxide, barium fluoride, cerium fluoride, magnesium fluoride, thorium fluoride, calcium fluoride, neodymium fluoride, lead fluoride, sodium fluoride, lithium fluoride, zinc selenide, zinc sulfide and mixtures thereof.

27. The product of Claim 25 wherein said third interlayer comprises a substantially optically transparent material selected from the group consisting of silicon nitride, titanium nitride, tantalum nitride, hafnium nitride, tungsten nitride, molybdenum nitride, zirconium nitride, boron nitride, silicon dioxide, silicon oxide,

WO 92/06843

PCT/US91/07209

-51-

yttrium oxide, germanium oxide, hafnium oxide, tungsten oxide, molybdenum oxide, boron oxide, tantalum oxide, titanium oxide, zirconium oxide, silicon carbide, germanium carbide, and mixtures thereof.

5 28. The product of Claim 27 wherein said third interlayer is at least 10 Å thick.

 29 The product of Claim 25 wherein said third interlayer comprises silicon dioxide at least 200 Å thick.

10 30. The product of Claim 29 wherein the thickness of said third interlayer is at least 200 Å.

 31. The product of Claim 25 wherein said third interlayer comprises a substantially optically transparent metallic material capable of reflecting visible light selected from the group consisting of silicon, germanium, 15 hafnium, molybdenum, tungsten, yttrium, tantalum, titanium and zirconium.

 32. The product of Claim 31 wherein said third interlayer is at least 25 Å thick.

20 33. The product of Claim 25 wherein said third interlayer comprises a substantially optically transparent metallic material capable of reflecting visible light selected from the group consisting of vanadium, niobium, chromium, manganese, rhenium, technetium, iron, cobalt, iridium, rhodium, nickel, palladium, platinum, copper, 25 silver, gold, zinc, ruthenium, indium, aluminum, tin, osmium, thallium, lead, antimony, bismuth and polonium.

 34. The product of Claim 33 wherein said third interlayer is at least 25 Å thick.

30 35. The product of Claim 25 wherein the thickness of at least one of said first interlayer, said third interlayer and said first diamond-like carbon layer is selected to minimize the reflection of light at predetermined wavelengths.

35 36. The product of Claim 25 wherein the thickness of at least one of said first interlayer, said third interlayer and said first diamond-like carbon layer is

WO 92/06843

PCT/US91/07209

-52-

selected to maximize the reflection of light at predetermined wavelengths.

37. The product of Claim 25 wherein the thickness of said first interlayer, said third interlayer and said first diamond-like carbon layer corresponds to integer multiples of quarter wavelength optical thickness at predetermined wavelengths.

38. The product of Claim 25 wherein the thickness of said third interlayer and said first diamond-like carbon layer corresponds to integer multiples of quarter wavelength optical thickness at predetermined wavelengths.

39. The product of Claim 25 wherein the compressive stress of said third interlayer is less than said first diamond-like carbon layer and greater than said adhesion-mediating layer.

40. The product of Claim 25 wherein said third interlayer exhibits a tensile stress and said first diamond-like carbon layer exhibits a compressive stress.

41. The product of Claim 25 including a fourth interlayer disposed between said third interlayer and said first diamond-like carbon layer of a substantially optically transparent material devoid of alkali metal atoms and fluorine and capable of forming a strong chemical bond with said third interlayer and said first diamond-like carbon layer.

42. The product of Claim 41 wherein said fourth interlayer comprises a substantially optically transparent material selected from the group consisting of silicon nitride, titanium nitride, tantalum nitride, tungsten nitride, molybdenum nitride, hafnium nitride, zirconium nitride, boron nitride, silicon dioxide, silicon oxide, yttrium oxide, germanium oxide, hafnium oxide, tantalum oxide, tungsten oxide, molybdenum oxide, boron oxide, titanium oxide, zirconium oxide, silicon carbide, germanium carbide and mixtures thereof.

43. The product of Claim 42 wherein said fourth

WO 92/06843

PCT/US91/07209

-53-

interlayer is at least 10 Å thick.

44. The product of Claim 41 wherein said fourth interlayer comprises silicon dioxide at least 200 Å thick.

45. The product of Claim 44 wherein the thickness of said fourth interlayer is at least 200 Å.

46. The product of Claim 41 wherein the thickness of at least one of said first interlayer, said third interlayer, said fourth interlayer and said first diamond-like carbon layer is selected to minimize the reflection of light at predetermined wavelengths.

47. The product of Claim 41 wherein the thickness of at least one of said first interlayer, said third interlayer, said fourth interlayer and said first diamond-like carbon layer is selected to maximize the reflection of light at predetermined wavelengths.

48. The product of Claim 41 wherein the thickness of said first interlayer, said third interlayer, said fourth interlayer and said first diamond-like carbon layer corresponds to integer multiples of quarter wavelength optical thickness at predetermined wavelengths.

49. The product of Claim 41 wherein the thickness of said third interlayer, said fourth interlayer and said first diamond-like carbon layer corresponds to integer multiples of quarter wavelength optical thickness at predetermined wavelengths.

50. The product of Claim 41 wherein the compressive stress of said fourth interlayer is less than said first diamond-like carbon layer and greater than said adhesion-mediating layer.

51. The product of Claim 41 wherein said fourth interlayer exhibits a tensile stress and said first diamond-like carbon layer exhibits a compressive stress.

52. The product of Claim 25 including at least one second composite layer bonded to and disposed immediately adjacent to said first composite layer.

53. The product of Claim 52 wherein the thickness

WO 92/06843

PCT/US91/07209

-54-

of at least one of said first interlayer, said third interlayer, said first diamond-like carbon layer, said second interlayer and said second diamond-like carbon layer is selected to minimize the reflection of light at
5 predetermined wavelengths.

54. The product of Claim 52 wherein the thickness of at least one of said first interlayer, said third interlayer, said first diamond-like carbon layer, said second interlayer and said second diamond-like carbon
10 layer is selected to maximize the reflection of light at predetermined wavelengths.

55. The product of Claim 52 wherein the thickness of said first interlayer, said third interlayer, said first diamond-like carbon layer, said second interlayer
15 and said second diamond-like carbon layer corresponds to integer multiples of quarter wavelength optical thickness at predetermined wavelengths.

56. The product of Claim 52 wherein the thickness of said third interlayer, said first diamond-like carbon
20 layer, said second interlayer and said second diamond-like carbon layer corresponds to integer multiples of quarter wavelength optical thickness at predetermined wavelengths.

57. The product of Claim 41 including at least one second composite layer bonded to and disposed
25 immediately adjacent to said first composite layer.

58. The product of Claim 57 wherein the thickness of at least one of said first interlayer, said third interlayer, said fourth interlayer, said first diamond-like carbon layer, said second interlayer and said second
30 diamond-like carbon layer is selected to minimize the reflection of light at predetermined wavelengths.

59. The product of Claim 57 wherein the thickness of at least one of said first interlayer, said third interlayer, said fourth interlayer, said first diamond-like carbon layer, said second interlayer and said second
35 diamond-like carbon layer is selected to maximize the

WO 92/06843

PCT/US91/07209

-55-

reflection of light at predetermined wavelengths.

60. The product of Claim 57 wherein the thickness of said first interlayer, said third interlayer, said fourth interlayer, said first diamond-like carbon layer, said second interlayer and said second diamond-like carbon layer corresponds to integer multiples of quarter wavelength optical thickness at predetermined wavelengths.

61. The product of Claim 57 wherein the thickness of said third interlayer, said fourth interlayer, said first diamond-like carbon layer, said second interlayer and said second diamond-like carbon layer corresponds to integer multiples of quarter wavelength optical thickness at predetermined wavelengths.

62. A chemical vapor deposition method for producing an abrasion wear resistant coated polymeric substrate product comprising: chemically degreasing the surface of a polymeric parent substrate; coating a substantially optically transparent polysiloxane polymer layer onto said parent substrate to a thickness of at least 3 microns; thermally curing said polysiloxane polymer coating; chemically cleaning the coated surface of said substrate; placing said substrate into a chemical vapor deposition reactor vacuum chamber and evacuating the air from said chamber to less than an approximately 5×10^{-6} Torr; sputter-etching the surface of said substrate with energetic gas ions at an energy of at least 200 eV to remove traces of residual hydrocarbon and to preferentially reduce the concentration of alkali metal atoms and alkali metal oxides at the substrate surface; chemically vapor depositing during a first cycle a substantially optically transparent first interlayer capable of forming a strong chemical bond to said substrate and diamond-like carbon onto to said substrate; chemically vapor depositing during said first cycle a substantially optically transparent diamond-like carbon layer having a thickness of at least 200 Å onto said

WO 92/06843

PCT/US91/07209

-56-

coated substrate; cooling said coated substrate by extinguishing said deposition process and passing an inert gas over said substrate until the temperature of said substrate has reached substantially room temperature during said cool down step; recovering a coated substrate product exhibiting superior resistance to abrasion and chemical attack.

63. The method of Claim 62 wherein the polysiloxane polymer coating step comprises a dip coating process.

64. The method of Claim 62 wherein the polysiloxane polymer coating step comprises a flow coating process.

65. The method of Claim 62 wherein the polysiloxane polymer coating step comprises a spray coating process.

66. The method of Claim 62 wherein the temperature of said parent substrate is maintained at less than 125°C during said chemical vapor deposition steps.

67. The method of Claim 62 wherein the thickness of said diamond-like carbon layer corresponds to integer multiples of quarter wavelength optical thickness at predetermined wavelengths.

68. The method of Claim 62 wherein the thickness of said first interlayer and said diamond-like carbon layer corresponds to integer multiples of quarter wavelength optical thickness at predetermined wavelengths.

69. The method of Claim 62 wherein the compressive stress of said first interlayer is less than said diamond-like carbon layer and greater than said adhesion-mediating layer.

70. The method of Claim 62 wherein said first interlayer exhibits a tensile stress and said diamond-like carbon layer exhibits a compressive stress.

71. The method of Claim 62 wherein at least a second cycle is used to chemically vapor deposit at least

WO 92/06843

PCT/US91/07209

-57-

a second interlayer and a second said diamond-like carbon layer onto said substrate.

72. The method of Claim 71 wherein the compressive stress of said first interlayer and said second interlayer is less than said diamond-like carbon layer and greater than said adhesion-mediating layer.

73. The method of Claim 71 wherein said first interlayer said second interlayer exhibit a tensile stress and said diamond-like carbon layer exhibits a compressive stress.

74. The method of Claim 71 wherein the deposition rate for said first interlayer, said second interlayer and said diamond-like carbon layer is generally in the range of about 0.1-10 microns/hour.

75. The method of Claim 62 wherein a third interlayer is chemically vapor deposited immediately adjacent to said first interlayer and away from said substrate of a substantially optically transparent material capable of forming a strong chemical bond to said first interlayer and a strong chemical bond to diamond-like carbon.

76. The method of Claim 75 wherein said diamond-like carbon layer is chemically vapor deposited immediately adjacent to said second interlayer and away from said substrate.

77. The method of Claim 75 wherein the deposition rate for said third interlayer is generally in the range of about 0.1-10 micron/hour.

78. The method of Claim 76 wherein the thickness of said third interlayer and said diamond-like carbon layer corresponds to integer multiples of quarter wavelength optical thickness at predetermined wavelengths.

79. The method of Claim 76 wherein the thickness of said first interlayer, said third interlayer and said diamond-like carbon layer corresponds to integer multiples of quarter wavelength optical thickness at predetermined

WO 92/06843

PCT/US91/07209

-58-

wavelengths.

80. The method of Claim 75 wherein the compressive stress of said third interlayer is less than said diamond-like carbon layer and greater than said
5 adhesion-mediating layer.

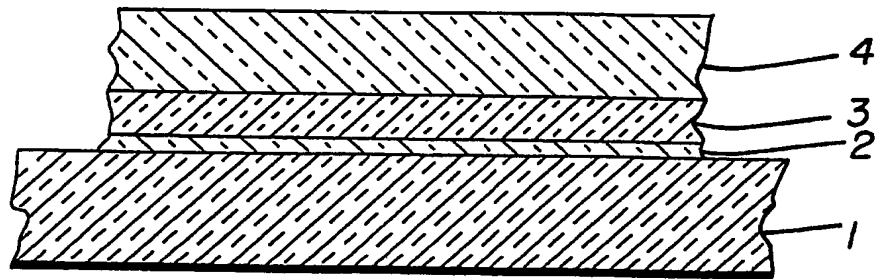
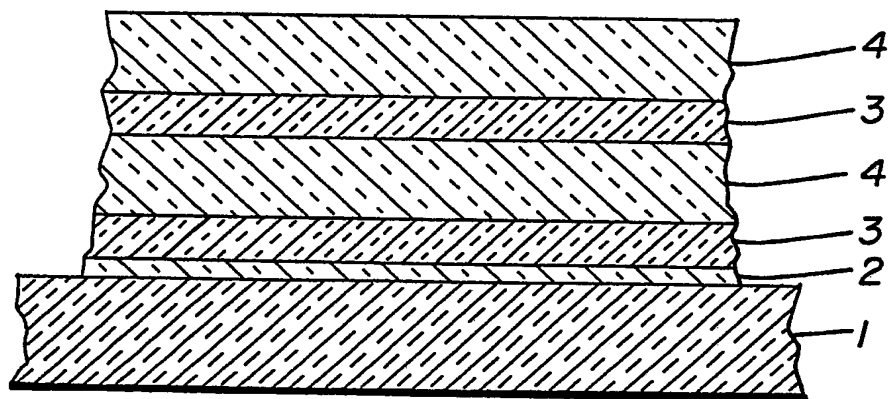
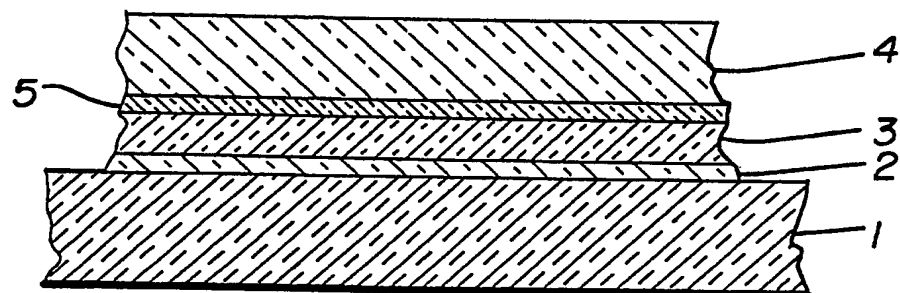
81. The method of Claim 75 wherein said third interlayer exhibits a tensile stress and said diamond-like carbon layer exhibits a compressive stress.

82. The method of Claim 75 wherein a second cycle
10 is used to chemically vapor deposit at least a second said first interlayer and a second said diamond-like carbon layer onto said coated substrate.

WO 92/06843

PCT/US91/07209

1/1

**FIGURE 1****FIGURE 2****FIGURE 3**

INTERNATIONAL SEARCH REPORT

PCT/US91/07209

International Application No.

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC(5): B32B 9/00, 7/02; C23C 16/02		
U.S. CL: 428/429, 408, 698, 472, 704, 216; 427/249, 255.7, 309, 398.1, 255.6		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
U.S.	428/216, 408, 429, 469, 472, 698, 704, 701, 702 427/249, 250, 255, 255.2, 255.7, 255.6, 309, 398.1, 419.1	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	US, A, 4,849,290 (FUJIMORI ET AL) 18 JULY 1989; See entire document.	1, 62
A	DD, A, 203 903 (GRIGULL) 09 NOVEMBER 1983; See the Abstract.	1, 62
A	US, A, 4,383,728 (LITINGTON) 17 MAY 1983; See column 1, lines 16-33.	1, 62
A	DD, A, 204 693 (BOLLINGER ET AL) 07 DECEMBER 1983; See the Abstract.	1, 62
A	JP, A, 61-55603 (CANNON KK) 20 MARCH 1986; See the Abstract.	1, 62
A	US, A, 4,847,157 (GOODMAN ET AL) 11 JULY 1989; See the Abstract.	1, 62
A	US, A, 4,734,339 (SCHACHNER ET AL) 29 MARCH 1988; See entire document.	1, 62
<p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Z" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
14 NOVEMBER 1991	24 DEC 1991	
International Searching Authority	Signature of Authorized Officer	
ISA/US	Archene A. Turner	

PCT/US91/07209

International Application No.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	JP, A, 64-2001 (IDEMITSU PETROCHEM KK) 06 JANUARY 1989; See the Abstract.	1, 62
A	JP, A, 61-106494 (KYOCERA CORP) 24 MAY 1986; See the Abstract.	1, 62
A	JP, A, 64-65092 (MATSUSHITA ELECTRICAL INDUSTRY CO. LTD.) 10 MARCH 1989 (TRANSLATION). See entire document.	1, 62
A	Appl. Phys. Lett., Vol. 55, No. 11, 11 SEPTEMBER 1989 (MA ET AL), "Selective nucleation and growth of diamond particles by plasma-assisted chemical vapor deposition," pages 1071-1073.	1, 62
A	Solid State Ionics 32/33 (1989), pages 861-868 (MOUSTAKAS), "THE ROLE OF THE TUNGSTEN FILAMENT IN THE GROWTH OF POLYCRYSTALLINE DIAMOND FILMS BY FILAMENT-ASSISTED CVD OF HYDROCARBONS"	1, 62
A	J. Vac. Sci. Technol. A 7(3), MAY/JUNE 1989, pages 2307-2310 (FRANKS), "Preparation and properties of diamondlike carbon films"	1, 62
Y	US, A, 4,661,409 (KIESER ET AL) 28 APRIL 1987; See entire document.	1-82